

PATENT SPECIFICATION

DRAWINGS ATTACHED

L161.039

1.161.039



Date of Application and filing Complete Specification: 23 Jan., 1960.
No. 3495/68.

Application made in United States of America (No. 618895) on 27 Feb., 1967.
Complete Specification Published: 13 Aug., 1969.

Index at acceptance:—G1 D7; H4 F(21C, 23L, 25R, 25X)

International Classification:—G 01 k 11/16

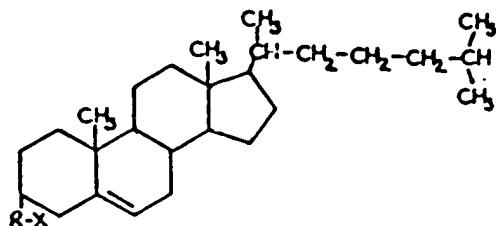
COMPLETE SPECIFICATION

A Visual Display Device

We, THE NATIONAL CASH REGISTER COMPANY of Dayton in the State of Ohio, and Baltimore in the State of Maryland, United States of America, a corporation organized under the laws of the State of Maryland, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to temperature-sensitive visual display devices and, more specifically, relates to such devices in the form of a dried emulsion coating having incorporated droplets of cholesteric mesomorphic ("liquid crystal") material, which material changes in iridescent characteristics where and when temperature changes occur on the coating.

The reflectance colour change phenomenon associated with certain types of so-called "liquid crystals" is well known. Most important in the class of "liquid crystals" which undergo spectral colour changes, iridescent in appearance, in conjunction with changes in temperature are certain cholesterol derivatives having the general structure:



where X represents a chemical linkage selected from oxy-, carbonyloxy-, and carbonyldioxy-linkages; and R represents a hydrocar-

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bon "residue" selected from the group comprising saturated or unsaturated alkyls, aryls, aryl-substituted alkyl, alkyl-substituted aryls, and halo- and nitro-substituted compounds derived from the above-named "R" materials. Other cholesterol derivatives which may be used include those wherein X, above, represents a halogen and R is excluded from the molecular structure. Each of these compounds can exist as a molecular mass in at least three physical phase configurations dependent upon the temperature of the material. Below a certain transitional temperature associated with a particular compound in a given environment circumstance, the cholesterol derivatives mass as a solid crystalline phase. Above another certain transitional temperature, the compounds exist in a liquid isotropic state with no regularity in molecular arrangement. In the change from the solid crystalline phase, having highly ordered molecular arrangement, to the liquid, isotropic, phase, having irregular, unordered molecular arrangement, as a function of temperature, there exists at least one mesophase; that is to say, a phase which is intermediate between the solid state and the liquid state. While a compound which exists in the above-referred-to mesomorphic state is commonly named a "liquid crystal", the term "mesomorph" is a more correct and descriptive title and will be used hereafter. There are three mesophases, the smectic, nematic and cholesteric mesophase, all of which may not exist for a given compound. The cholesteric material in a mesophase is a liquid, molecularly isotropic, continuous structure in which are randomly distributed domains of aligned molecules in spaced layers adapted to reflect a probing incident light. A general discussion of mesophases and mesomorphic compounds is found in the publication "Molecular Structure and the Properties of Liquid Crystals", by G. W.

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Gray, published in 1962 by Academic Press, New York and London. Under proper conditions within a certain temperature range, the domains of aligned molecules in the cholesteric mesophase mass are capable of affecting a probing incident light in such a manner that the probing light is reflected in a distinctive spectral hue, usually in bands, dependent on temperature, giving, in most instances, an iridescent effect, depending on the quality of the incident light.

A particularly efficient method for providing a system having this spectral or iridescent effect is the provision of thin films of mesomorphic materials which can exist as a cholesteric mesophase on a substrate which is either opaque or transparent, coloured or not. For an effective visual display of the iridescence of these materials, a film of a thickness of a few thousandths of an inch can be employed, and this affords suitable contrast when supported on a black, opaque substrate. Such a substrate allows no dilution of the emanating iridescent light by reflectance from the substrate or backlighting by transmitted light, and has the added advantage of appearing black in incident light at temperatures above and below those required to yield the cholesteric mesomorphic state.

The usual colour effect obtained from a film of cholesteric-mesomorphic material is a brilliant colour pattern composed of bands or areas of spectral colour ranging from red to blue. The colours are a function of temperature change in the film, the system generally yielding relatively shorter wavelengths as the temperature rises, although exceptions have been noted in the literature in which the wavelengths of emanating light lengthens as temperature is raised. Of course, above and below the temperatures necessary for visual colour display there is reflection of ultraviolet and infrared wavelengths of greater or lesser extent, depending upon the system being studied and the quality of incident light.

With few exceptions, the systems chosen for temperature detection and display in a particular use are compounds of two or more mesomorphic compounds selected and combined for the purpose of causing colour change within a specified temperature range.

While mixtures of these cholesterol derivatives yield workable film systems, it is a general rule that the temperature at which colour is produced in the use of such structures is not the colour producing temperature noted for each material used alone, but will generally be lower than the temperature at which the material having the highest temperature parameters first yields colour, and sometimes may be lower than the colour producing temperature of the material having the lowest temperature parameters.

Until recently, the utility of cholesteric mesomorphs in temperature-sensitive systems

has been severely limited due to a number of reasons, the following points being some of the assigned faults:

(1) such systems containing a mixture of one or more interdigitated mesomorphic compounds as a film are subject to crystallization of large areas at the desired working temperatures. This undesirable crystallization needs to concentrate one of the active materials at each crystallization site to thereby separate it from the other components of such a mesomorphic mixture. This component separation results in (a) loss of precision and efficiency in colour change at the desired temperature, and (b) anomalous colour change activity at other temperatures; 70

(2) mesomorphic cholesterol derivatives are oily liquids at and above their melting temperatures. When they exist as a film on any surface, the film, being wet, is subject to injury of many types from ageing and contact with the environment. Dust particles are easily entrapped by the liquid surface and can serve as undesirable nucleation sites for crystallization. Such films are exposed to the danger of contact with any material in the vicinity, with resultant disorganization of the mesomorph and possible change in thickness in localized areas, which would alter the response of the system; and 80

(3) the subject wet-film mesomorphic systems are prone to anomalous colour change behaviour upon the event of only slight contamination of the system by various solutes. This contamination can cause iridescence by itself at a given temperature not otherwise associated with the yield of colour in the film generally, or it can produce large shifts in the colour producing temperature, either higher or lower. 90

In the specification of United Kingdom pending Patent Application No. 23569/67 (Serial No. 1138590) a display device is disclosed and claimed which includes an array of minute polymeric capsules containing cholesteric mesomorphic material and adhered to a substrate whose temperature pattern is to be displayed. 100

While somewhat related to the use of the above-mentioned capsule arrays, an emulsion of unencapsulated cholesteric mesomorphic material, which is a part of the subject matter of this invention, is vastly different from these other disclosures in several important respects. The droplets of the material of this invention are not encapsulated but are inclusions in the continuous phase of the emulsion. The emulsion, of coating liquid, of this invention can be prepared by a simple and inexpensive, one-step, process, thereby ob-

viewing the necessity for complex capsule-manufacturing equipment and techniques with attendant high manufacturing costs. The emulsion of this invention, when dried at a coating on a body whose temperature pattern is to be displayed, provides that incident light be transmitted through only a single kind of material in order to be reflected iridescently from the unencapsulated droplets of cholesteric mesomorphic material. Due to the extremely small droplet size which can be maintained in an emulsion of unencapsulated droplets of the cholesteric mesomorphic materials, coatings prepared from an emulsion permit of a high degree of optical resolution and also have a very smooth surface.

Thus, according to the invention, there is provided a visual display device comprising a continuous film of polymeric material having dispersed therein minute droplets of a liquid material capable of assuming a cholesteric mesophase in a predetermined temperature range, said polymeric material transmitting light incident thereon and reflected from the droplets of said liquid material.

Materials which can be used as a film-forming polymeric material in the emulsion of this invention include any polymeric material which is soluble in a liquid which does not dissolve or substantially chemically affect the liquid crystal material to be emulsified therein. Another, obvious, requirement of the film-forming material is that the polymeric material, in its dried state, transmit enough light to make use of the colour reflectance characteristics of the liquid crystal material inclusions. Representative examples of a few such film-forming polymeric materials include gelatin, gum arabic, poly(vinyl alcohol), poly(vinylpyrrolidone), poly(ethylene oxide), poly(ethylene - co - maleic anhydride), poly(vinyl methyl ether - co - maleic anhydride) and poly(acrylate).

Films prepared by drying the emulsion of this invention, which contain the liquid droplets, can be strained or tinted, if desired, to serve as a colour filter for light travelling to and from the cholesteric mesomorphic material. Such a film system would find use where a narrowing of the broad iridescent effect is desired. If they fit an intended purpose, films prepared by the teaching of this invention can also be slightly pigmented. However, care must be exercised in the amount of pigment or non-light reflecting material used in the emulsion, because an excessive amount will work to the detriment of brilliance in the colour response due to absorption of and interference with the incident and reflected light.

Dried emulsion films can be either self-supporting or not, as desired or as most fitting to the purpose at hand. In the use of a self-supporting or free-standing film of the dried emulsion, that is, film not having a sub-

strate, wherein the film is not opaque or non-light-reflecting, there should be direct contact of the film with the body whose temperature pattern is to be exhibited to obtain the most dramatic results. Lack of such direct contact between the film and the test body results not only in an incorrect display of temperature-pattern discontinuities, but also in greatly reduced brilliance of the colour reflectance due to "return-deflectance" of incident light from the back-side of the film material. Non-opaque temperature pattern display films or similar translucent films for which more brilliant colour response is desired can be coated on one flat surface with appropriate non-light-reflecting materials either black or of any selected colour. Supported films of the dried emulsion can have as a substrate any suitable material, thick or thin, coloured or not, transparent or opaque. A film formed by coating the emulsion onto a test body having an irregular surface and dried thereon is considered to be a supported film with a substrate, as the term "film" relates to thickness and not to smoothness or regularity.

In the accompanying drawings the same reference numerals relate to the same parts.

Figure 1a is a diagrammatic edge view of a substrate sheet 10 having, on one surface, a coating of minute droplets 11 of liquid crystal material dispersed in a matrix-like polymeric binder material 12, the liquid crystal material being shown in either the isotropic liquid state or the crystalline solid state; that is, not in the mesomorphic state;

Figure 1b shows the coated substrate sheet 10 of Figure 1a with the liquid crystal material 11 in the mesomorphic state. Figure 1a is intended to represent the film coating at a temperature above or below that which is required for colouration of the mesomorph-containing film material, while Figure 1b is to represent the same film coating within the temperature range of colouration. The hatching of the droplets in Figure 1b is used to depict a colour change from that of Figure 1a and not to suggest particular colours, because iridescence cannot well be suggested by hatching. The coated film can be of a thickness to include only a single layer or a few layers of liquid crystal droplets, or the film can include several layers of droplets within its thickness. Droplets of liquid crystal material can range in size from about five microns to about twenty-five microns and are preferably ten to twenty microns in diameter. Depending upon conditions and requirements for use of the intended coating, several layers which include liquid crystal material of different temperature response ranges can be superimposed in direct or overlapping relation on a surface; or discrete areas of a surface can be coated with layers which include different types of liquid crystal

material to obtain temperature response corresponding to the coated pattern and the material coated;

Figure 2 is a diagrammatic edge view of a self-supporting film containing minute droplets 11 of a single type of liquid crystal material dispersed in a matrix of polymeric binder material 12. Although the film is depicted as having a thickness of only a few droplets diameters, in practice the film may be of any thickness extending from slightly more than one droplet diameter at its thinnest extreme up to gross dimensions of several millimeters. The optional coloured layer 13 shown in this figure as well as in Figures 1a and 1b and in Figure 3, to follow, may be provided or not, as desired, its purpose being to colour and/or opacify one surface of the film and thereby act as a background for observing the hue or to enhance the colour brilliance of the display; and

Figure 3 is a diagrammatic edge view of a self-supporting film containing minute droplets 11 of more than one type of liquid crystal material dispersed in a matrix of polymeric binder material 12. The figure depicts two different types of liquid crystal material contained within the film coating, a first type, for which the ambient film temperature is either above or below the temperature of its mesomorphic state, and a second type, which exists in the mesomorphic state at the film temperature of this figure. It is understood that more than just two different types of liquid crystal material may be included in a film.

Following are examples of specific embodiments of the invention which are presented to demonstrate techniques used in practice of the invention. It is understood that these examples are not intended to limit, in any way, the scope of this invention.

EXAMPLE I

In this example, a mixture of the specified liquid crystal materials was used which consisted of 55%, by weight, oleyl cholesteryl carbonate and 45%, by weight, cholesteryl nonanoate and had a colour producing temperature, in the upward excursion, of about 33 degrees centigrade. The temperature range of colour response for this mixture was from about 33 degrees centigrade to about 35.5 degrees centigrade. Three parts, by weight, of the above mixture of liquid crystal material were emulsified in a Waring Blender with five parts, by weight, of a 10% by weight, aqueous solution of poly(vinyl alcohol) described below, until a liquid crystal droplet size-range of from about five microns to about twenty microns was obtained. The poly(vinyl alcohol) used in this example had an average molecular weight of 88,000 and was characterized by the facts that (a) a 4%, by weight, aqueous solution of the material exhibited a viscosity

of 23 to 28 centipoises at 25 degrees centigrade, and (b) the material was 97.7% to 98.4% hydrolyzed; that is, that specified percentage of acetate chemical groups originally present in molecules of the subject material had been converted to hydroxyl groups.

The emulsion, once prepared, was coated by means of a draw-down applicator, to a wet-film thickness of about ten mils onto a blackened substrate sheet of polyethylene terephthalate. The film was allowed to dry in air at about 25 degrees centigrade. If the temperature of the coating was raised at a point, concentric rings representing a temperature gradient pattern in the range of from 33 degrees centigrade to 35.5 degrees centigrade appeared outwardly from a central ring of blue, thence spectrally in order through red, as the temperature gradient decreased. As the temperature of the point was increased or decreased, the effect was evidenced by expansion or contraction of the rings. Systems of adjacent expanding and contracting rings from two or more points intersected, and the resultant colour of an area was a function of the temperature of that area.

The dried emulsion film of this example can be stripped from its polyethylene terephthalate substrate and utilized as an unbacked film for displaying temperature gradient patterns. The stripped film can be blackened or opacified on one surface, or it can be used without such blackener or opacifier, as desired.

EXAMPLE II

In this example, a mixture of liquid crystal material was used which consisted of 50%, by weight, oleyl cholesteryl carbonate and 50%, by weight, cholesteryl nonanoate. Three parts of the liquid-crystal mixture were emulsified with five parts of a 1%, by weight, aqueous solution of gelatin having suitable film strength. Emulsified droplets of liquid crystal material ranged in size from about ten microns to about twenty microns.

The emulsion, once prepared, was coated, with the use of a draw-down applicator, onto a substrate sheet of polyethylene terephthalate to a wet-film thickness of about ten mils. The so-coated film was dried in air at about 25 degrees centigrade. The resulting film exhibited temperature response characteristics similar to those of the film in Examples I, and the colour producing temperature was observed to be about 25 degrees centigrade, with 25 to 30 degrees centigrade as the temperature range for complete spectral colour change.

The dried film of this example can be stripped from its substrate and used in the same manner as the film in Example I.

EXAMPLE III

In this example, one part, by weight, of the same liquid crystal mixture as was used

in Example II was emulsified in five parts, by weight, of a 22%, by weight, aqueous solution of poly(acrylate) polymeric material. The poly(acrylate) material was ammonium poly(acrylate) and was characterized by having a pH of 8.5 to 9.5 in a 22%, by weight, aqueous solution and by having a viscosity of 150 to 250 centipoises in a 5%, by weight, aqueous solution. Emulsification was conducted in a jacketed Waring Blender cup equipped with a resistance-wire heater, and the temperature of the emulsified liquid was maintained at 50 degrees centigrade. Liquid crystal droplets in the emulsion were ten to twenty 15 microns in diameter.

The emulsion, once prepared, was coated and dried as described in Example II, and behaviour of the dried film was noted to be essentially identical to that of Example II 20 with respect to colour change according to change in temperature, since the liquid crystal mixture was the same in both example, the dried binder seemingly having little effect as to light-response. A coating was also prepared using glass as the substrate, and results 25 were comparable to those described above.

EXAMPLE IV

This example was provided to demonstrate an embodiment of the subject invention wherein in the polymeric binder material, which serves 30 to secure droplets of liquid crystal material in dispersion in the matrix, is coloured to reduce its transparency to incident light. The coloured matrix-like material of this example, thereby, effectively contrasts with the iridescence of entrapped liquid crystal droplets without reliance on opaque substrates or other applied contrasting material.

Three parts, by weight, of a mixture of 40 85%, by weight, of cholesteryl nonanoate and 15%, by weight, oleyl cholesteryl carbonate were emulsified with five parts, by weight, of a coloured binder solution, described below, in a jacketed Waring Blender cup which 45 was controlled to maintain the liquid temperature at about 50 degrees centigrade. To prepare the binder solution, 10 grams of the poly(vinyl alcohol) specified in Example I was dissolved in 90 millilitres of water, and to the 50 solution was added 10 millilitres of fountainpen black ink.

The emulsion, having been prepared with droplets of liquid crystal material of about five to twenty-five microns in size, was coated 55 to a wet-film thickness of ten mils onto a transparent, uncoloured, sheet of polyethylene terephthalate, using a draw-down applicator as in Example I, and the coating was allowed to dry in air at about 25 degrees 60 centigrade. The dried emulsion film could be used either as a thin self-supporting film stripped from its substrate or together with the substrate to provide durability. Change in temperature of the film in the presence of

incident light resulted in the characteristic colour change, which first became evident for this mixture of liquid crystal materials as the temperature rose to about 55 degrees centigrade, iridescence being caused by a variation in temperature over the film area.

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EXAMPLE V

The materials used in this example were identical with those in Example IV. In this example, however, the emulsion was sprayed onto a substrate by means of a spray gun, and the resulting dried film demonstrated colour-reflecting characteristics similar to those of Example IV.

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EXAMPLE VI

In this example, the polymeric binder material was zein, a prolamine film-former derived from the alcohol extraction of zea mays, a grain commonly called Indian corn. The solvent system utilized in this example was a solution of nine parts, by volume, of methanol and one part by volume of water. A solution of binder material was prepared by dissolving 80 grams of zein in 400 millilitres of the solvent system.

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An emulsion was prepared in a jacketed Waring Blender cup controlled to maintain a temperature of about 50 degree centigrade. The emulsion consisted of 50 millilitres of the binder material solution and 10 millilitres of a one-to-one mixture of oleyl cholesteryl carbonate and cholesteryl nonanoate.

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The emulsion was coated as in Example II, and results were similar to those of Example II with regard to iridescent effect.

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EXAMPLE VII

This example demonstrates the use of an emulsion which has two different types of liquid crystal materials separately included therein. The emulsion-coating liquid system was prepared by stirring together two emulsions which had different liquid crystal materials emulsified in separate solutions of the same kind of binder material. The two emulsions were prepared as follows:

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- 25 millilitres of 10%, by weight, aqueous poly(vinyl alcohol) solution (as used in Example I) was emulsified with 15 grams of a mixture of 65%, by weight, of oleyl cholesteryl carbonate and 35%, by weight, cholesteryl nonanoate, and
- 25 millilitres of the 10%, by weight, aqueous poly(vinyl alcohol) was emulsified with 15 grams of a mixture of 85%, by weight, cholesteryl nonanoate and 15%, by weight oleyl cholesteryl carbonate.

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The two emulsions were then stored together carefully and by hand, it being discovered that undue agitation in combining these particular emulsions causes mixing to-

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nature of the droplets of liquid crystal material.

5 The emulsion-coating system with two different liquid crystal materials, was coated onto a substrate and dried in the air at about 25 degrees centigrade.

10 The visual effect of a coated dried emulsion of this example was much the same as that of the previous examples, except that colour change appeared in the coating in two sequence, beginning at two different temperatures. As a comparison to the visual effect described in Example I, for a coating having only one liquid crystal material, the following describes a coating with two liquid crystal materials. In warming a test point on the film, a first sequence of concentric rings of colour appeared, circling the point of heat application. When the point on the film was further warmed above the first colour producing temperature but below the colour producing temperature of the second emulsified material, the test point again appeared uncoloured, with only a ring of colour remaining, at that time, a fixed distance from the centre of the heat source, due to the static temperature gradient. Upon further warming of the test point on the film, a second set of colour rings began to appear and move outwardly, but never reached the outwardly-moving first rings, giving rise to a visual indication of two temperature ranges at different locations on the coated substrate. So much for point application of heat. When the coated substrate, as a whole, was heated, the film reflected changing colour not in rings, but all over, colours first appearing due to one liquid crystal material and then, on further heating, the film appearing uncoloured, due to the second liquid crystal material, for a time at temperatures intermediate to the different colour producing temperatures. The colour changes appeared in reverse order on cooling of the film.

15 45 Where, in a given small area, there are present two kinds of the liquid drops which exhibit different colour reflectance at a given temperature, the effect on the eye is additive, as would be expected.

WHAT WE CLAIM IS:-

50 1. A visual display device comprising a continuous film of polymeric material having dispersed therein minute droplets of a liquid material capable of assuming a cholesteric mesophase in a predetermined temperature range, said polymeric material transmitting light incident thereon and reflected from the droplets of said liquid material.

55 2. A display device according to Claim 1, wherein the said liquid material consists of a mixture of cholesterol derivatives, octyl cholestryl carbonate being one cholesterol derivative in the mixture.

60 3. A display device according to Claim 1, wherein the said liquid material consists of a mixture of cholesterol derivatives, cholestryl nonanoate being one cholesterol derivative of the mixture.

65 4. A display device according to Claim 1, wherein the said film of polymeric material contains more than one kind of liquid material droplets differing from one another by their different temperature response.

70 5. A display device according to any one of the preceding claims, wherein said continuous film of polymeric material is coated onto a substrate.

75 6. A display device according to Claim 5, wherein the substrate is substantially non-light-reflecting.

80 7. A display device according to Claim 6, wherein the substantially non-light-reflecting substrate is black.

85 8. A display device according to any one of the preceding claims, wherein the droplets of said liquid material range in size from five microns to twenty five microns.

90 9. A visual display device substantially as hereinbefore described with reference to the accompanying drawings.

10. A method of making a visual display device substantially as hereinbefore described in Examples I to VII.

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Agent for the Applicants.

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1 SHEET

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FIG.1a.

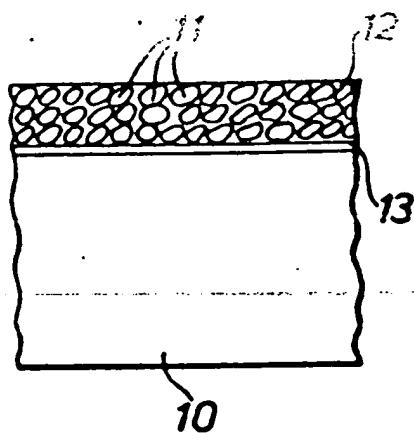


FIG.1b.

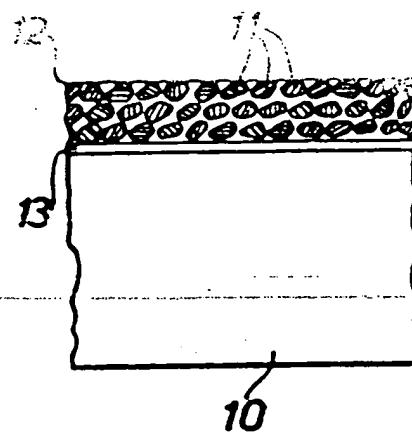


FIG.2.

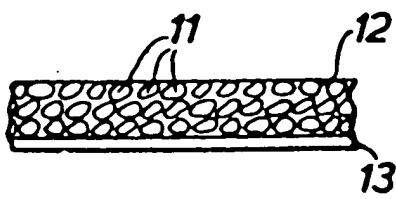
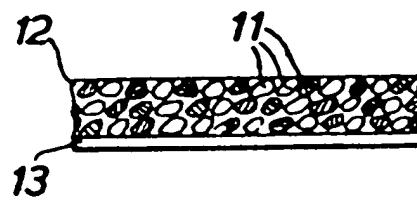


FIG.3.



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